

FORM PTO-1390 (REV 11-2000)	U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER <b>124-910</b>
<b>TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371</b>		U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.5) <b>09/980711</b> unknown
INTERNATIONAL APPLICATION NO. <b>PCT/GB00/02179</b>	INTERNATIONAL FILING DATE <b>05/06/2000</b>	PRIORITY DATE CLAIMED <b>17/06/1999</b>

TITLE OF INVENTION

**PROCESS FOR PRODUCING A LITHIUM TRANSITION METAL SULPHIDE**

APPLICANT(S) FOR DO/EO/US

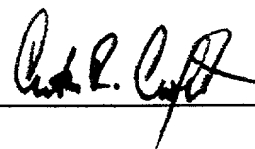
**RITCHIE, A. et al.**

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☐ The U.S. has been elected by the expiration of 19 months from the priority date (Article 31).
5. A copy of the International Application as filed (35 U.S.C. 371(c)(2)).
  - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
  - b. ☒ has been communicated by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
  - a. ☐ is attached hereto.
  - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
  - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ have been communicated by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has **NOT** expired.
  - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

**Items 11 To 20 below concern document(s) or information included:**

11. ☒ An Information Disclosure Statement under 37 C.F.R. 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 C.F.R. 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
14. ☐ A SECOND or SUBSEQUENT preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821-1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information. PTO Form 1449, Intl Search Report and 2 Cited References

U.S. APPLICATION NO. <b>097/980711</b>		INTERNATIONAL APPLICATION NO <b>PCT/GB00/02179</b>		ATTORNEY'S DOCKET NUMBER <b>124-910</b>															
21. <input checked="" type="checkbox"/> The following fees are submitted:				<b>CALCULATIONS PTO USE ONLY</b>															
<b>BASIC NATIONAL FEE (37 C.F.R. 1.492(a)(1)-(5):</b> -- Neither international preliminary examination fee (37 C.F.R. 1.482) nor international search fee (37 C.F.R. 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO .....\$1040.00 -- International preliminary examination fee (37 C.F.R. 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO .....\$890.00 -- International preliminary examination fee (37 C.F.R. 1.482) not paid to USPTO but international search fee (37 C.F.R. 1.445(a)(2)) paid to USPTO .....\$740.00 -- International preliminary examination fee (37 C.F.R. 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) .....\$710.00 -- International preliminary examination fee (37 C.F.R. 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) .....\$100.00  <b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				\$	890.00														
				\$	0.00														
				Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 C.F.R. 1.492(e)).															
				\$	0.00														
				<table border="1" style="width:100%; border-collapse: collapse;"> <thead> <tr> <th style="width:20%;">CLAIMS</th> <th style="width:20%;">NUMBER FILED</th> <th style="width:20%;">NUMBER EXTRA</th> <th style="width:20%;">RATE</th> </tr> </thead> <tbody> <tr> <td>Total Claims</td> <td style="text-align: center;">10</td> <td style="text-align: center;">-20 =</td> <td style="text-align: center;">0</td> </tr> <tr> <td>Independent Claims</td> <td style="text-align: center;">2</td> <td style="text-align: center;">-3 =</td> <td style="text-align: center;">0</td> </tr> <tr> <td colspan="3">MULTIPLE DEPENDENT CLAIMS(S) (if applicable)</td> <td style="text-align: center;">\$280.00</td> </tr> </tbody> </table>		CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	Total Claims	10	-20 =	0	Independent Claims	2	-3 =	0	MULTIPLE DEPENDENT CLAIMS(S) (if applicable)	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE																
Total Claims	10	-20 =	0																
Independent Claims	2	-3 =	0																
MULTIPLE DEPENDENT CLAIMS(S) (if applicable)			\$280.00																
<b>CLAIM FEES ARE NOT BEING PAID AT THIS TIME TOTAL OF ABOVE CALCULATIONS =</b>				\$	890.00														
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$	0.00														
<b>SUBTOTAL =</b>				\$	890.00														
Processing fee of \$130.00, for furnishing the English Translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 C.F.R. 1.492(f)).				\$	0.00														
<b>TOTAL NATIONAL FEE =</b>				\$	890.00														
Fee for recording the enclosed assignment (37 C.F.R. 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 C.F.R. 3.28, 3.31). <b>\$40.00</b> per property				\$	40.00														
Fee for Petition to Revive Unintentionally Abandoned Application (\$1280.00 - Small Entity = \$640.00)				\$	0.00														
<b>TOTAL FEES ENCLOSED =</b>				\$	930.00														
				Amount to be:															
				refunded	\$														
				Charged	\$														
a. <input checked="" type="checkbox"/> A check in the amount of \$930.00 to cover the above fees is enclosed. b. <input type="checkbox"/> Please charge my Deposit Account No. 14-1140 in the amount of \$_____ to cover the above fees. A duplicate copy of this form is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 14-1140. A duplicate copy of this form is enclosed. d. <input checked="" type="checkbox"/> The entire content of the foreign application(s), referred to in this application is/are hereby incorporated by reference in this application.																			
<b>NOTE: Where an appropriate time limit under 37 C.F.R. 1.494 or 1.495 has not been met, a petition to revive (37 C.F.R. 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</b>																			
<b>SEND ALL CORRESPONDENCE TO:</b>  NIXON & VANDERHYE P.C. 1100 North Glebe Road, 8 <sup>th</sup> Floor Arlington, Virginia 22201-4714 Telephone: (703) 816-4000																			
				 SIGNATURE															
				Arthur R. Crawford NAME															
				25,327 REGISTRATION NUMBER															
				December 5, 2001 Date															

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

#4/a

In re Patent Application of

RITCHIE, A. et al.

Atty. Ref.: 124-910

Serial No. unknown

Group:

Filed: December 5, 2001

Examiner:

For: PROCESS FOR PRODUCING A LITHIUM TRANSITION METAL SULPHIDE

\* \* \* \* \*

December 5, 2001

Assistant Commissioner for Patents  
Washington, DC 20231

Sir:

**PRELIMINARY AMENDMENT**

In order to place the above-identified application in better condition for examination, please amend the application as follows:

**IN THE SPECIFICATION**

Please substitute the following paragraphs in the specification for corresponding paragraphs previously presented. A copy of the amended specification paragraphs showing current revisions is attached.

**IN THE CLAIMS**

Please substitute the following amended claims for corresponding claims previously presented. A copy of the amended claims showing current revisions is attached.

**IN THE SPECIFICATION**

Page 1, before the first line, insert as a separate paragraph:

This application is the U.S. national phase of international application  
PCT/GB00/02179 filed June 5, 2000, which designated the U.S..

**IN THE CLAIMS**

4. A process according to claim 1 further comprising the step of recovering sulphur from the product.
7. A lithium transition metal sulphide obtainable by a process according to claim 1.

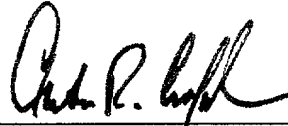
REMARKS

Attached hereto is a marked-up version of the changes made to the specification and claims by the current amendment. The attached page(s) is captioned "Version With Markings To Show Changes Made."

Respectfully submitted,

NIXON & VANDERHYE P.C.

By: \_\_\_\_\_



Arthur R. Crawford  
Reg. No. 25,327

ARC:ecb  
1100 North Glebe Road, 8th Floor  
Arlington, VA 22201-4714  
Telephone: (703) 816-4000  
Facsimile: (703) 816-4100

**VERSION WITH MARKINGS TO SHOW CHANGES MADE**

**IN THE SPECIFICATION**

Page 1, before the first line, insert as a separate paragraph:

This application is the U.S. national phase of international application  
PCT/GB00/02179 filed June 5, 2000, which designated the U.S..

**IN THE CLAIMS**

4. A process according to ~~any one of the preceding claims~~ 1 further comprising the step of recovering sulphur from the product.
7. A lithium transition metal sulphide obtainable by a process according to ~~any one of the preceding claims~~ 1.

PROCESS FOR PRODUCING A LITHIUM TRANSITION METAL SULPHIDE

The present invention relates to processes for the production of sulphides, in particular lithium transition metal sulphides useful in the production of batteries, and to the use of molten sulphur as a solvent in such processes.

In the 1980's, there was extensive research into lithium metal rechargeable batteries, particularly using sulphides, but also selenides, as cathode materials. Many lithium metal / molybdenum disulphide ( $\text{Li/MoS}_2$ ) batteries were produced but these were withdrawn following an incident in which a fire was attributed to the malfunction of such a battery. Other sulphides, such as iron disulphide  $\text{FeS}_2$ , titanium disulphide  $\text{TiS}_2$  and selenides, such as niobium triselenide  $\text{NbSe}_3$  have also been particularly investigated as alternative cathode materials.

Although the use of lithium metal rechargeable batteries is now limited for reasons of safety, they are still used in the laboratory testing of materials. Lithium metal primary batteries using iron disulphide cathodes are manufactured.

Virtually all modern lithium rechargeable batteries are of the lithium - ion type, in which the negative electrode (anode) comprises lithium absorbed into a carbon support. These use a lithium containing cathode material, which is usually lithium cobalt oxide  $\text{LiCoO}_2$  although lithium nickel oxide  $\text{LiNiO}_2$ , lithium manganese oxide  $\text{LiMn}_2\text{O}_4$  and mixed oxides are also known to have been used.

Due to their high cost, the use of lithium rechargeable batteries at present is mainly limited to premium applications, such as portable computers or telephones. To gain access to wider markets, for example in applications such as the powering of electric vehicles, the cost must be reduced. Hence there is a strong demand for the high performance obtainable from lithium - ion batteries at much more economical prices.

On first inspection, the use of sulphides as cathode materials is not as attractive as the use of oxides. This is because the voltage achievable from sulphides is generally only about half of that achievable using corresponding oxides. However, the capacity of batteries incorporating sulphide based cathodes, measured in ampere hours per gram of material, is about 3 times greater than corresponding batteries incorporating oxide based cathodes. This leads to an overall advantage of about 1.5 times in terms of cathode energy density for batteries with sulphide based cathodes. A further advantage is that iron sulphides, in particular ferrous sulphide ( $\text{FeS}$ ), are inexpensive materials which may be dug out of the ground as natural occurring

minerals. By contrast, lithium cobalt oxide is an expensive material, due mainly to the high cost of cobalt metal.

Binary transition metal sulphides are however not suitable for direct use in lithium - ion cells as they do not contain lithium. Lithium transition metal ternary sulphides, such as lithium molybdenum sulphide, lithium titanium sulphide, lithium niobium sulphide and lithium iron sulphide have been suggested as electrode materials for batteries (see for example, Japanese Kokai No 10208782 and Solid State Ionics **117** (1999) 273 - 276). The conventional synthesis of lithium iron sulphide is via a solid state reaction in which lithium sulphide,  $\text{Li}_2\text{S}$ , and ferrous sulphide,  $\text{FeS}$ , are intimately mixed together and heated under an inert atmosphere at a temperature of ca.  $800^\circ\text{C}$ . The reaction is diffusion controlled and the kinetics are slow. Consequently, the reaction can take up to 1 month at temperature to reach completion. This is highly inconvenient and is costly in terms of energy input. The economics of this synthesis for battery production are clearly unfavourable.

On a laboratory scale, lithium iron sulphide can be made by an electrochemical synthesis route in which a lithium metal / iron disulphide cell is discharged, and the lithium metal is removed and replaced by a carbon anode. This process however, is not amenable to scaling up. A further laboratory synthesis of lithium iron sulphide is the solid state reaction of lithium nitride,  $\text{Li}_3\text{N}$ , with iron disulphide,  $\text{FeS}_2$ , but again, this method is unsuitable for large scale use because of the high cost and shock sensitivity of lithium nitride.

The applicants have developed an economical synthesis which can be operated on a large scale to produce sulphides, or mixtures of sulphides, which have useful electrochemical properties.

In accordance with the present invention a process for the production of a lithium transition metal sulphide comprises reacting a transition metal sulphide with lithium sulphide in a solvent comprising molten sulphur.

Suitably the transition metal sulphide used in the process is an iron, molybdenum, niobium or titanium sulphide and is preferably an iron sulphide. Ferrous sulphide,  $\text{FeS}$  is an inexpensive and readily available naturally occurring mineral.

Preferably the reaction is carried out at a temperature of between  $95.5^\circ\text{C}$  and  $444^\circ\text{C}$ . This is sufficient to melt the sulphur in order to allow it to act as solvent.

The reaction proceeds more rapidly than previously known processes. On a laboratory scale, the reaction can be completed in a few hours, with the actual reaction time dependent largely on the heating time of the furnace.



Although lithium sulphide may be bought commercially, for large scale production it is more economical to produce lithium sulphide via the reduction of lithium sulphate. One convenient method is to heat lithium sulphate above its melting point of 860°C in the presence of carbon. Other standard reduction methods may  
5 equally be used, as well known in the art.

The sulphur used as the solvent is inexpensive, but it is preferably recovered from the product and reused. This may be achieved by dissolving it out of the product using a solvent. A suitable solvent is carbon disulphide, which can also be recovered and recycled if desired. Alternatively, sulphur can be removed by vapourisation, for  
10 example by heating the product/sulphur mixture above the boiling point of sulphur; which is 444°C at atmospheric pressure. A temperature in the region of 500°C is suitable.

Lithium transition metal sulphides obtained by the above described process form a further aspect of the invention. These may comprise a single lithium transition  
15 metal sulphide phase or a mixture of lithium transition metal sulphide phases and are useful in the production of electrodes for use in batteries. In particular, they are useful in the production of electrodes for rechargeable batteries. These electrodes form the cathode, and suitable anodes are lithium ion anodes as are known in the art. Suitable electrolytes are also well known and include mixtures of inorganic carbonates, for  
20 example ethylene carbonate, propylene carbonate, diethyl or dimethyl carbonates, ethyl methyl carbonate together with a lithium salt, usually lithium hexafluorophosphate,  $\text{LiPF}_6$ , or lithium trifluoromethane sulphonate ('triflates'),  $\text{LiCF}_3\text{SO}_3$  or lithium tetrafluoroborate,  $\text{LiBF}_4$ .

Molten sulphur is not a conventional solvent in a chemical reaction, and  
25 therefore this forms a further aspect of the invention. As described above, it is particularly suitable for use as a solvent in chemical reactions used in the production of sulphides, such as lithium transition metal sulphides.

The invention will now be particularly described by way of example only with reference to the accompanying diagrammatic drawing, Figure 1, which shows the  
30 charge/discharge (cycling) curve of a battery containing a cathode prepared using the material obtained by the process of the invention.

#### Example

##### Synthesis of lithium iron sulphide

35 Equimolar amounts of lithium sulphide,  $\text{Li}_2\text{S}$ , and ferrous sulphide,  $\text{FeS}$ , were intimately mixed with an excess of sulphur. This mixture was put into a tube furnace

and heated to a temperature of 150°C under an inert atmosphere of argon. The furnace was held at this temperature for about an hour after which time the temperature was increased to 500°C in order to remove the excess sulphur by vapourisation. After cooling, the product was removed from the furnace and stored in an inert atmosphere glove box, to avoid reaction with moisture in air.

The product was analysed using X - ray powder diffraction which showed that the main phases present were lithium iron sulphides of various compositions,  $\text{Li}_3\text{Fe}_2\text{S}_4$ ,  $\text{Li}_7\text{Fe}_2\text{S}_6$  and  $\text{Li}_2\text{FeS}_2$ , with a small amount of iron disulphide (pyrites),  $\text{FeS}_2$ . This material was then tested for use in laboratory cells as described previously in A. Gilmour, C. O. Giwa, J. C. Lee and A. G. Ritchie, Lithium Rechargeable Envelope Cells, Journal of Power Sources, volume 65, pp 219 - 224 (1997), Power Sources 16. The lithium iron sulphide was made into a battery cathode by preparing a slurry of it with a binder, ethylene propylene-diene monomer (EPDM) dissolved in cyclohexane together with a conductive additive of carbon. This slurry was then coated onto a support using a doctor blade coating technique to form a cathode.

The cathode was electrically cycled against an anode of graphite using an electrolyte of ethylene carbonate/diethylcarbonate/ lithium hexafluorophosphate,  $\text{LiPF}_6$ . Charge/discharge (cycling) curves are illustrated in Figure 1. This shows that the product could be charged and discharged using standard conditions.

20

CLAIMS

1. A process for producing a lithium transition metal sulphide, the process  
5 comprising reacting a transition metal sulphide with lithium sulphide in a solvent  
comprising molten sulphur.
2. A process according to claim 1; wherein the transition metal sulphide is an iron,  
molybdenum or titanium sulphide.  
10
3. A process according to claim 2; wherein the transition metal sulphide is an iron  
sulphide.
4. A process according to any one of the preceding claims further comprising the  
15 step of recovering sulphur from the product.
5. A process according to claim 4; wherein the sulphur is recovered by dissolution  
in a solvent.
- 20 6. A process according to claim 4; wherein the sulphur is recovered by  
vapourisation.
7. A lithium transition metal sulphide obtainable by a process according to any  
one of the preceding claims.  
25
8. A battery comprising an electrode containing a lithium transition metal sulphide  
according to claim 7.
9. The use of molten sulphur as a solvent in a chemical reaction for the production  
30 of a sulphide.
10. The use according to claim 9; wherein the sulphide is a lithium transition metal  
sulphide.

1/1

Fig.1.  
Li-ion  $\text{Li}_x\text{Fe}_y\text{S}_z$  cell cycling  
( $0.5\text{mA}/\text{cm}^2$ )

